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by

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INTRODUCTION

At present, synthetic crude oil is produced from two commercial operations which process bitumen from Athabasca oil sands in northern Alberta. Bitumen upgrading is achieved by coking processes. The polycyclic aromatic ring structures of the material are cracked to a lighter product which is then fractionated into coker distillates and upgraded further by severe hydrotreating which removes sulphur and nitrogen and also saturates olefins and some aromatics. The degree of aromatic saturation is a function of the process severity and much of the middle distillate produced from Athabasca oil sand syncrudes is high in aromatics and deficient in hydrogen. Diesel fuels which are produced from highly aromatic feedstocks have poor ignition qualities and jet fuels from these sources cause overheating in turbo engines resulting in increased maintenance costs. Blending of synthetic with conventional crudes is the current practice for accommodating unconventional feedstocks in refinery operations and the amount blended is a function of the total product slate. Canadian refineries are usually limited to a synthetic crude intake of between 20-30% and middle distillate fuels are usually the limiting factor.

Adding hydrogen to saturate aromatics and convert them to naphthenes has been practised by refineries for some time. The degree of conversion depends on factors such as temperature, pressure, residence time, catalyst and aromatic type. High hydrogen partial pressures and long residence times will improve the degree of conversion but operating at high temperatures may be counterproductive since the hydrogenation reaction may be limited by the approach to thermodynamic equilibrium. Catalysts used are typically those employed in hydrotreating for sulphur and nitrogen removal, i.e. nickel-molybdenum, cobalt-molybdenum and nickel-tungsten on alumina. The development of more active and durable catalysts is needed to improve the efficiency of aromatic saturation processes. More active catalysts would allow less severe operating regimes and enhance the economic feasibility of these processes.

It is important to note that although saturation of aromatics may improve the hydrogen/carbon ratio of synthetic distillates, the disparity of paraffins in these fuel sources is a fundamental problem and increasing the naphthene content may only marginally increase the combustion requirements of a fuel. The feedstock used in this study may be seen as an example since the aromatic content has been reduced significantly by severe hydrotreating during primary upgrading but the product does not meet the cetane number specification for diesel fuel.

The purpose of this study was to produce quality diesel fuel from the feedstock by further hydrotreating to reduce the level of aromatics. The aim was to establish the degree of conversion required to achieve the specified cetane number rating. It was also desirable to compare the activity of the hydrotreating catalysts since the literature contains little work on catalyst development for aromatic saturation in this type of feedstock. Finally, it was necessary to investigate the effect of thermodynamic equilibrium on the aromatic saturation process and to establish the optimum operating conditions which may be used as a basis for future work.

EXPERIMENTAL

The feedstock was a middle distillate fraction cut from a synthetic crude oil which was produced by delayed coking of Athabasca bitumen. The properties of the feedstock are given in Table 1. Two catalysts were used for hydroprocessing the feed. Catalyst A was a typical commercial $CoO-MoO_3/\gamma-Al_2O_3$ and catalyst B a commercial $NiO-WO_3/\gamma-Al_2O_3$. The properties of the catalysts are presented in Table II.

A detailed description of the catalyst-testing system has been presented previously (1). Experimental runs were carried out using a bench-scale continuous flow reactor operating in the up-flow mode. Liquid feed and hydrogen were mixed, passed through a pre-heater and then over a fixed bed of catalyst. The reactor was 0.025 m in internal diameter, 0.305 m long, of total volume 155 cc and made of 316 stainless steel. The reactor furnace consisted of three separately controlled heating zones and the heat input to each zone was controlled so that the catalyst bed was maintained at a constant isothermal temperature. The axial temperature profile was measured by a movable thermocouple located in a thermo-well mounted centrally in the reactor. For each experimental run the reactor was filled sequentially from the bottom with 42 cc of berl saddles, 100 cc of catalyst extrudates or spheres and 13 cc of berl saddles. Each catalyst loading was 70 grams. The catalyst was sulphided at 380°C and atmospheric pressure by passing a mixture of 10% H_2S in hydrogen over the bed for 2 hours. The amount of H_2S passed was equivalent to eight theories of sulphur. A theory is defined as the stoichiometric quantity of sulphur required to convert the known quantities of Co, Ni, Mo and W present to their corresponding sulphides. Immediately after sulphiding, the reactor was pressured with hydrogen ready for the first run. The unit was run for 8 hours on oil before the first steady-state sample was taken.

For all experimental runs the reactor pressure was maintained at 17.2 MPa (2500 psig). (This condition was chosen because the feedstock was previously hydrotreated in primary upgrading at 10.3 MPa (1500 psig) over a $NiO-MoO_3/\gamma-Al_2O_3$ catalyst). Experimental runs were performed at temperatures of 340-440°C, liquid space velocities of 0.75 to 2.25 hr^{-1} and a hydrogen flow rate at STP of 530 L hydrogen per L of feedstock (3000 scf/bbl). The reactor system was maintained at steady-state conditions for 1 hr prior to and 2 hr during the period in which product was collected. The hydrotreated product was analyzed for aromatic carbon content by C^{13} NMR analysis using a Varian XL-200 spectrometer. Sulphur content was analyzed by the Wickbold technique and carbon, hydrogen and nitrogen analysis was carried out using a Perkin Elmer 240B analyzer. The average molecular weight of the feedstock was determined with a Knauer vapour pressure osmometer. The catalyst total pore volume was determined with a Micromeritics Model 910 mercury porosimeter. The mean reactor residence time for aromatic saturation was calculated from a knowledge of the total voidage of the catalyst bed, the hydrogen flow rate and the average molecular weight of the feed. Complete vaporization of feed on contacting the catalyst bed was assumed.

TABLE 1

PROPERTIES OF MIDDLE-DISTILLATE FEEDSTOCK

Relative Density, 15/15°C	0.836
Carbon	87.46 wt %
Hydrogen	12.47 wt %
Sulphur	0.055 wt %
Nitrogen	54 ppm
Average Molecular Weight	201
% Aromatic Carbon by C^{13} NMR	14.3
Cetane Number	35
Distillation (D86)	
IBP °C	142
10%	181
50%	232
90%	283
FBP	333

TABLE II

CATALYST PROPERTIES

Catalyst

A $CoO-MoO_3/\gamma-Al_2O_3$,
(Cyanamid Aero Trilobe HDS-20)
Containing: 10.8 wt % Mo and 3.9 wt % Co
Surface area 230 m^2/g
Pore volume 0.43 cc/g
Extrudates of 2.5 mm average diameter

B $NiO-WO_3/\gamma-Al_2O_3$
(Katalco Sphericat NT-550)
Containing: 15.8 wt % W and 3.9 wt % Ni
Surface area 200 m^2/g
Pore volume 0.58 cc/g
Spheres of 0.32 mm average diameter

RESULTS AND DISCUSSION

Effect of Thermodynamic Equilibrium on Aromatic Saturation

A high degree of aromatic saturation of a middle-distillate may be achieved using a single-stage hydrotreating unit operating under severe process conditions. However, the conversion to naphthenes is a reversible reaction and involves a chemical equilibrium which is temperature dependent:

$$\text{Aromatic} + n\text{H}_2 \rightleftharpoons \text{Naphthene} \qquad 1)$$

At high temperatures the degree of conversion may therefore be limited by the approach to thermodynamic equilibrium. Because of this limiting factor it is important to find the optimum operating conditions.

Since aromatic compounds generally have higher relative densities than their corresponding naphthenes we expect the relative density to decrease with the degree of conversion. The relative density of hydrotreated distillate determined for each experimental run was plotted as a function of LHSV for each reaction temperature. The results for the two catalysts are presented in Figure 1. It is found that the values show a steady decrease with reaction temperature, the effect being greater for catalyst A. Thus, with increase in temperature the values do not pass through a minimum as would be expected and we are led to believe that the decrease in relative density at the higher temperatures is due to cracking of the distillate to lighter products.

Figures 2 and 3 show the effect of change of LHSV on the % aromatic carbon in the product over the complete temperature range. For both catalysts all curves show a minimum at a temperature value which is between 380-400°C. Above this temperature the effect of thermodynamic equilibrium is observed as the % aromatic carbon begins to increase again. At any operating condition the degree of aromatic conversion was significantly greater using catalyst B. The maximum conversion was achieved at 380°C and 0.75 LHSV. Under these conditions the aromatic carbon content was reduced to 0.41% corresponding to a 97% conversion.

The cetane number of this sample was found to be 42 and within the specification limit of 40.

Kinetics of Aromatic Saturation

The equilibrium reaction given by Equation 1 is the basis for elucidating the reaction kinetics. Two simplifying assumptions are also made:- (i) the forward reaction is assumed to be pseudo-first-order since the hydrogenation is carried out in large hydrogen excess at constant partial pressure; (ii) the reverse reaction is also assumed to be first-order in naphthene carbon.

The aromaticity of the feedstock is defined as the percentage of aromatic carbon ($\%C_A$) as determined by C^{13} NMR. The fraction of carbon atoms which are aromatic is therefore given by $A = \% C_A/100$. Similarly the fraction of naphthene carbon atoms is given by $N = \% C_N/100$. The rate expression for the reversible reaction is then

$$-\frac{dA}{dt} = k_1 A(P_{H_2})^n - k_1' N \qquad 2)$$

where k_1 and k_1' are the forward and reverse rate constants and P_{H_2} is the hydrogen partial pressure.

Introducing assumption (i) Equation 2 becomes

$$-\frac{dA}{dt} = k_f A - k_1' N \qquad 3)$$

where $k_f = k_1 (P_{H_2})^n$ = constant.

If A_o and N_o are the fractions of aromatic and naphthene carbon atoms respectively at residence time $t = 0$, then N may be expressed in terms of A, A_o and N_o by a simple mass balance. At equilibrium the forward and reverse reaction rates are equal and the equilibrium constant is given by

$$K = \frac{k_f}{k_1'} = \frac{N_e}{A_e} \qquad 4)$$

Where A_e and N_e are the equilibrium fractions of aromatic and naphthene carbons respectively and K is the equilibrium constant. With the usual working for a first-order-reversible reaction it may be shown that

$$-\frac{dA}{dt} = k_f \frac{(K + 1)}{K} (A - A_e) \qquad 5)$$

Putting $k_r = k_f (K + 1)/K$ and integrating we obtain the final expression

$$\ln \frac{A - A_e}{A_o - A_e} = -k_R t \qquad 6)$$

The equilibrium aromatic fractions were calculated from the literature using the data of Wilson et al (2) and Frye (3). Figures 3 and 4 present pseudo-first-order plots for the catalysts A and B respectively. The rate constants for catalyst B were found on average to be greater than A by a factor of two. The pseudo-rate-constants, k_R, were determined from the data by regression-analysis and used in the Arrhenius equation

$$\ln k_R = \ln A - E/RT \qquad 9)$$

Where A is the Arrhenius pre-exponential factor, E is the activation energy and R the gas constant. Arrhenius plots are presented in Figure 6. Regression-analysis gave values of the activation energy of 15.0 ± 2.3 and 14.2 ± 0.9 kcal/g-mol for catalysts A and B respectively and these values agree within experimental error. They also compare favourably with the value of 17 kcal/g-mol obtained by Voorhoeve and Stuiver for benzene hydrogenation over sulphided nickel-tungsten on alumina at 300-400°C (4).

CONCLUSIONS

Saturation of aromatics in a middle-distillate from an Athabasca synthetic crude oil was achieved by severe hydroprocessing. The optimum operating conditions were found such that a 97% aromatic conversion was obtained using a sulphided nickel-tungsten on alumina catalyst. The cetane number of the non-aromatic diesel fuel was found to be 42 and within the specification limit. A sulphided cobalt-molybdate on alumina catalyst was found to be significantly less active and gave reaction rates which were half those obtained for the nickel-tungsten catalyst.

ACKNOWLEDGMENTS

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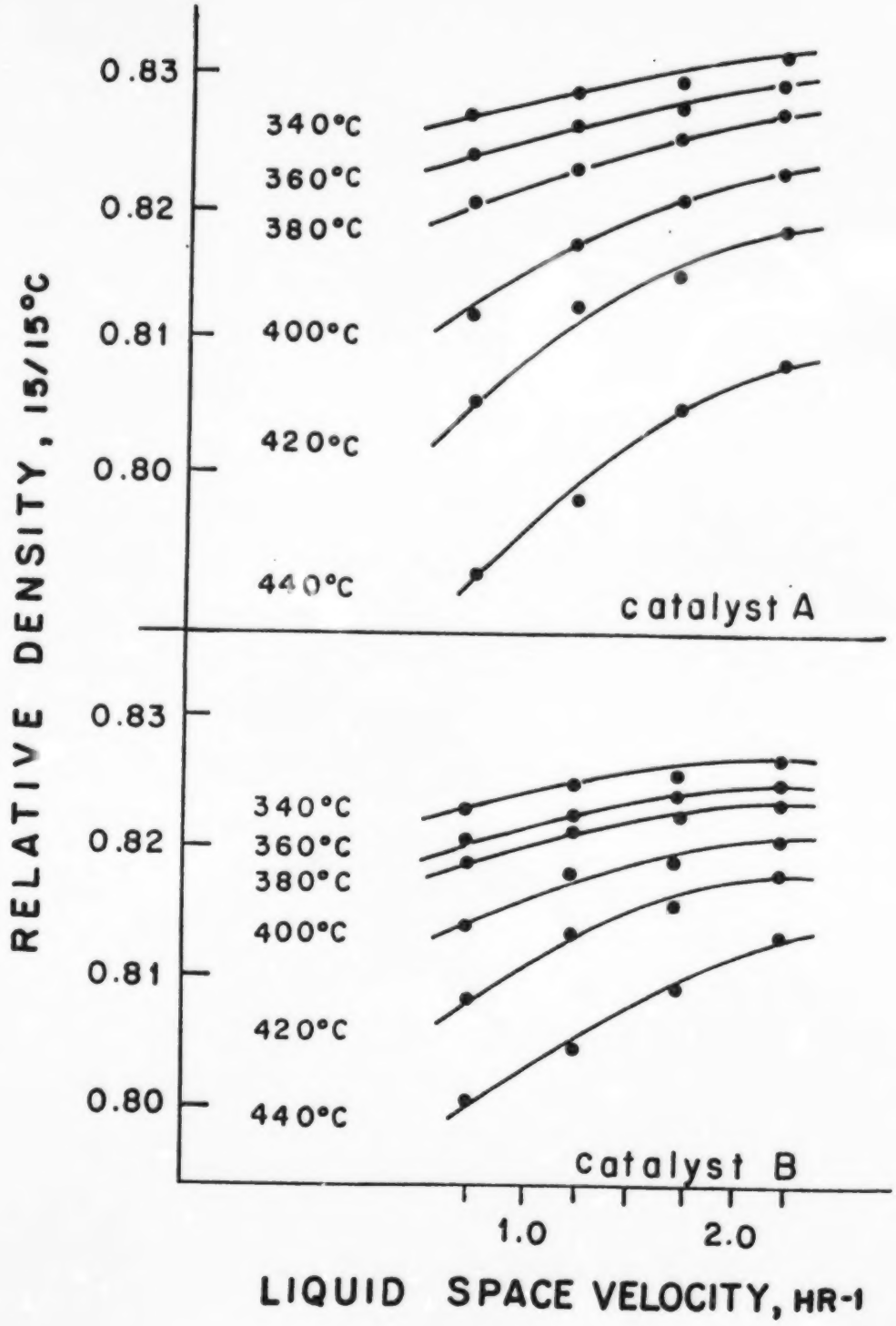

FIGURE 1. PLOTS OF RELATIVE DENSITY OF PRODUCT Vs. LIQUID SPACE VELOCITY

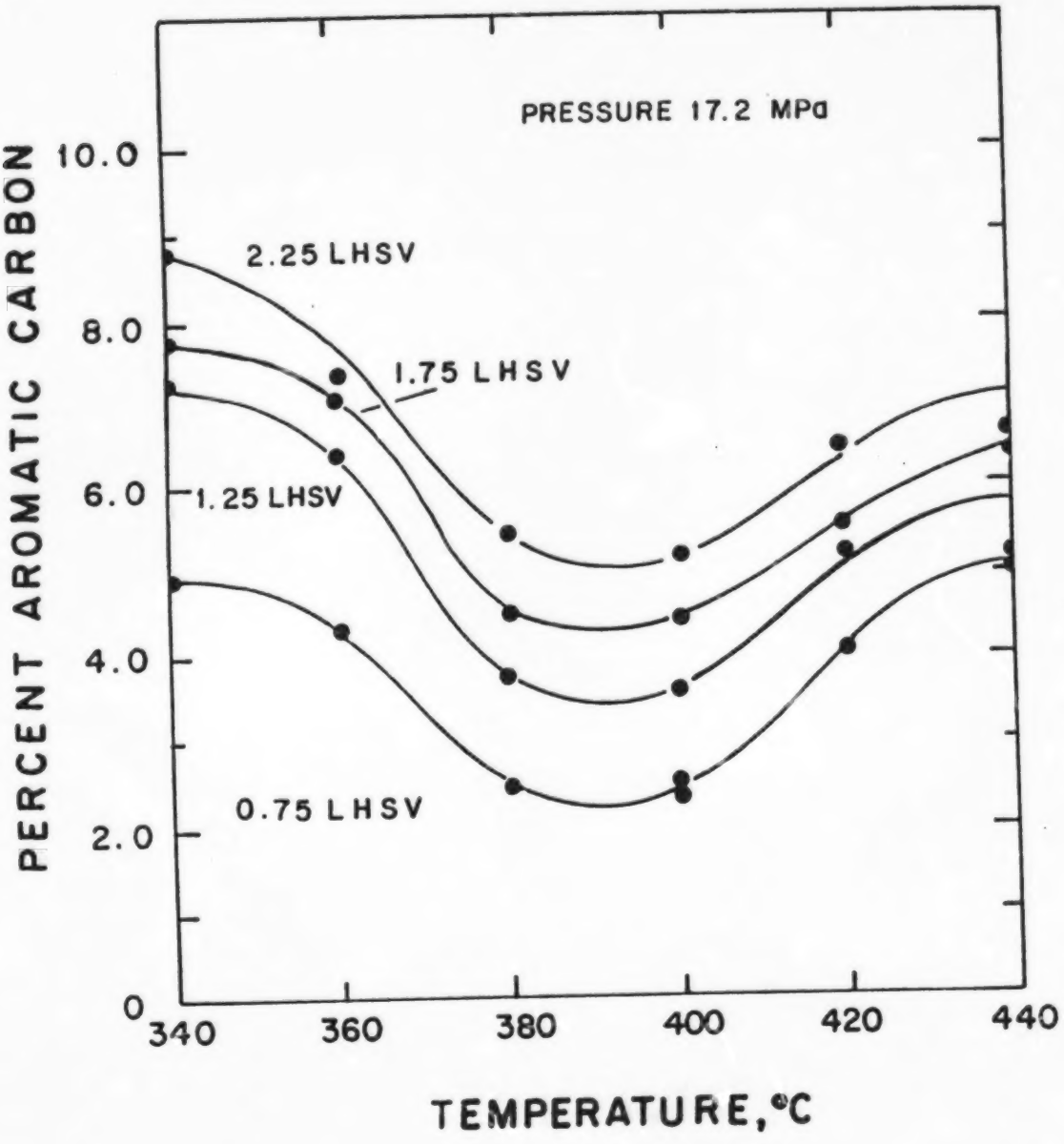

FIGURE 2. EFFECT OF LHSV ON AROMATICS SATURATION OVER CATALYST A.

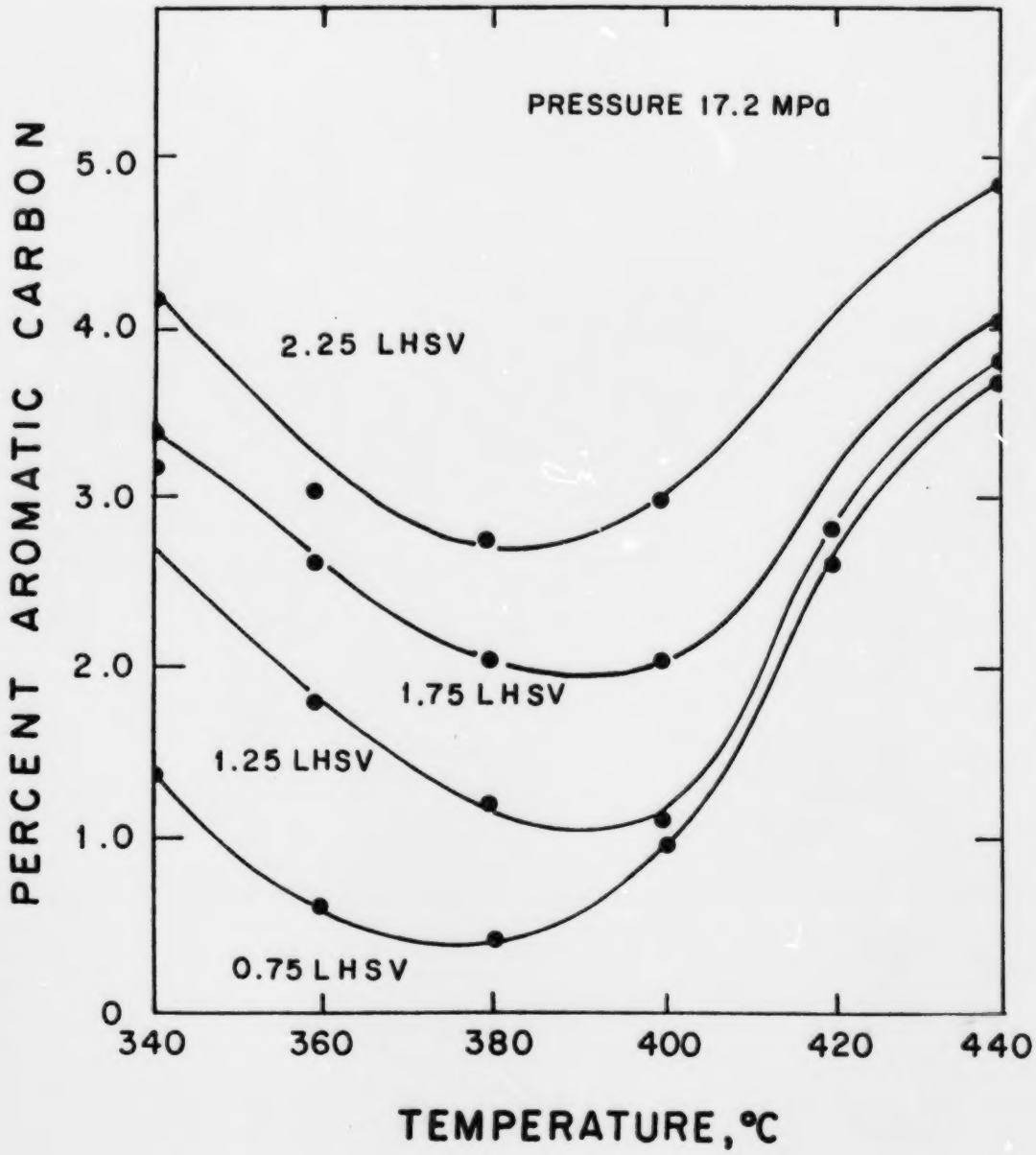

FIGURE 3. EFFECT OF LHSV ON AROMATICS SATURATION OVER CATALYST B.

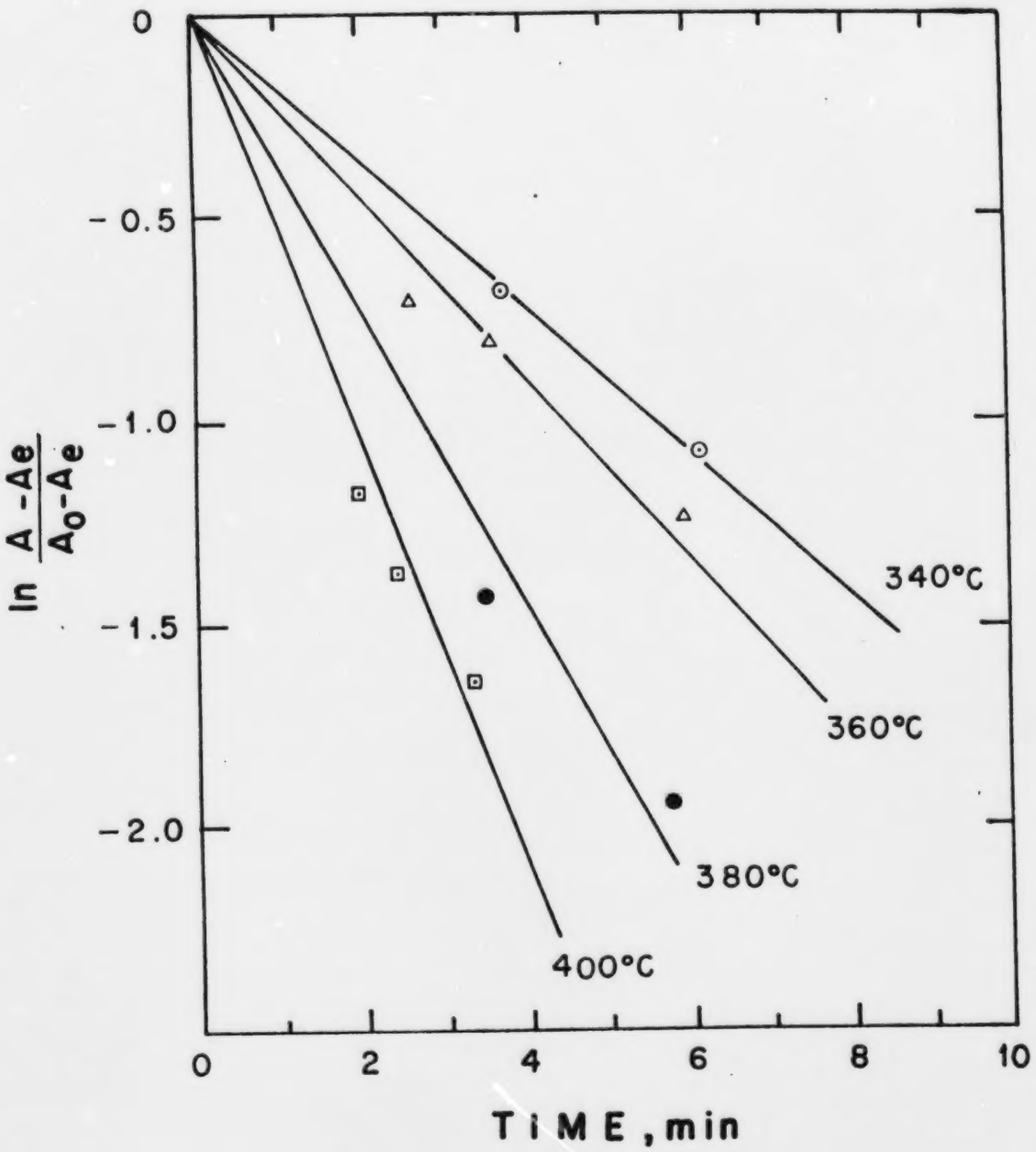

FIGURE 4. PSEUDO-FIRST-ORDER REVERSIBLE KINETICS FOR REACTION OVER CATALYST A.

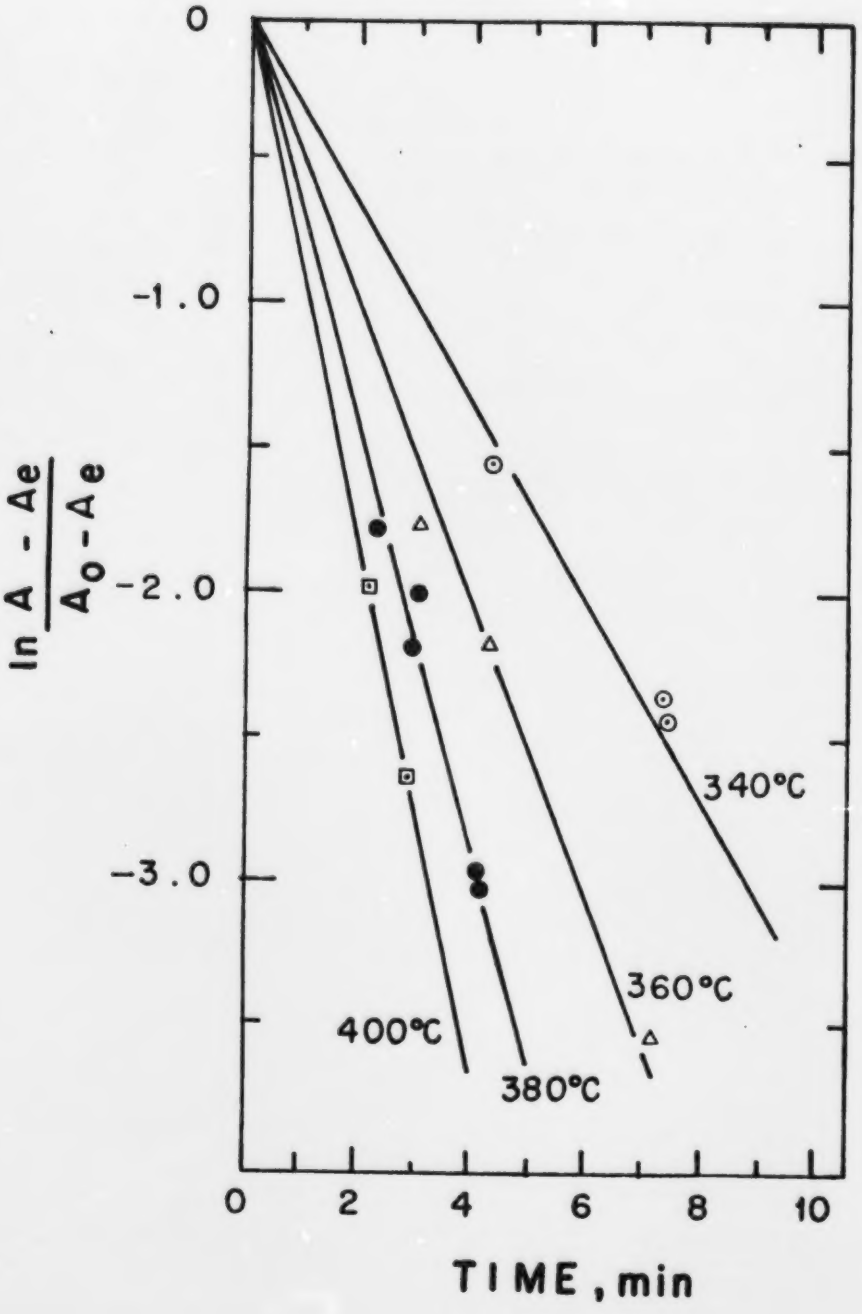

FIGURE 5. PSEUDO-FIRST-ORDER REVERSIBLE KINETICS FOR REACTION OVER CATALYST B.

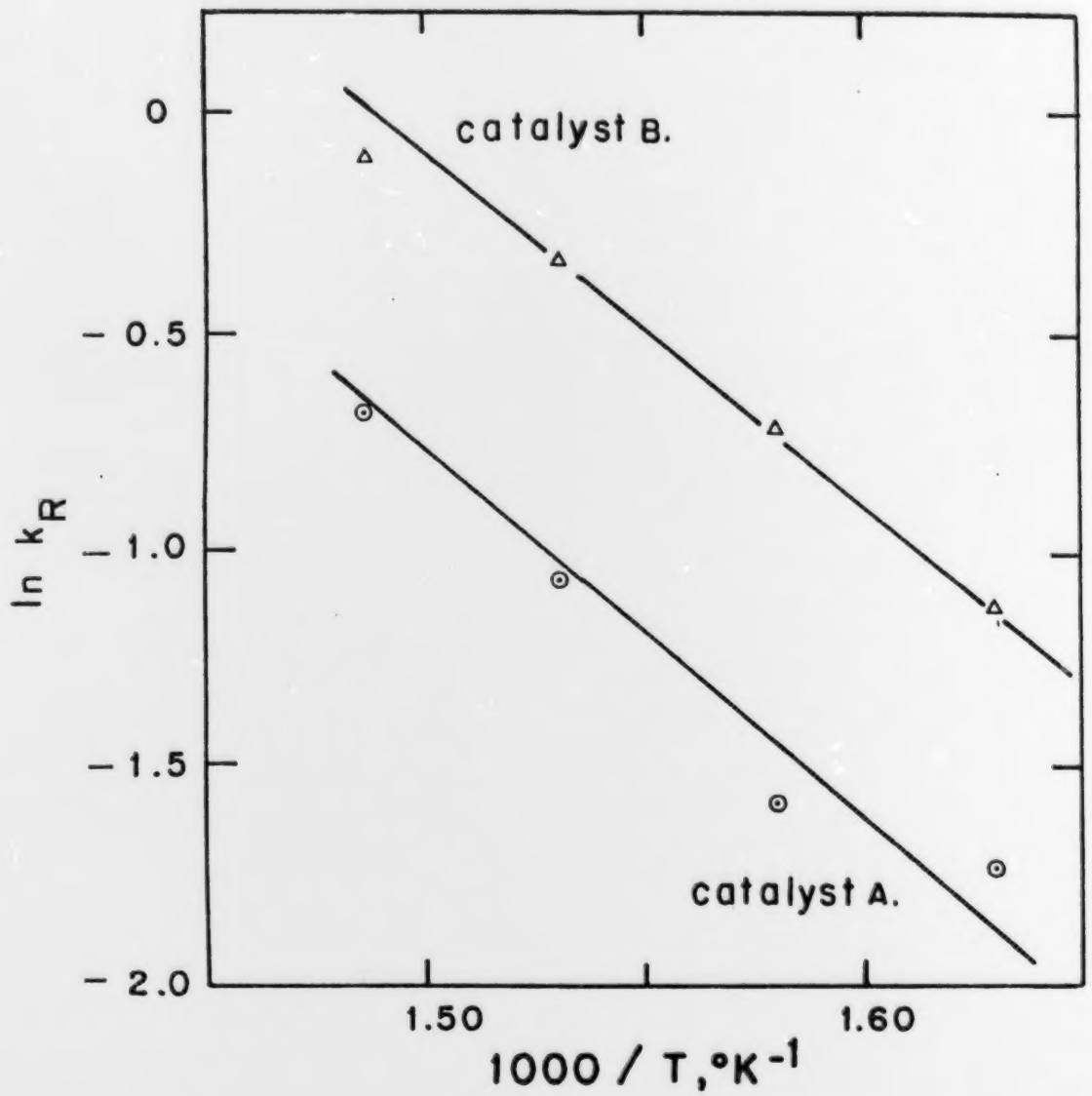

FIGURE 6. ARRHENIUS PLOT OF PSEUDO - RATE CONSTANTS FOR AROMATICS SATURATION